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(54) MOLDING COMPOSITIONS OF REINFORCED POLYAMIDES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to molding compositions of polyamides reinforced with mineral fillers and having improved surface properties.

It is well known to reinforce thermoplastic polyamides with mineral fillers to increase rigidity, hardness and dimensional stability and reduce water absorption. Such reinforced polymeric molding compositions are described, for example, in German Published Application 1,520,392.

However, such molding compositions suffer from the drawback that when they are injection molded, for example, the surface of the molding is uneven and has a matt appearance. This is probably due to the accumulation of filler at the surface, which accumulations cannot be removed until the processing temperature has reached such a high value that degradation of the polymer occurs or the molten polymer becomes so fluid that undesirable fins (flashes) are produced on the injection molding.

The present invention seeks to provide polyamide molding composition reinforced with mineral fillers and capable of being processed to shaped articles having a satisfactory glossy surface.

German Patents 1,066,736 and 1,197,615 disclose that the surface of shaped articles of polyamide may be improved by the addition of small amounts of, say, amine derivatives or salts of higher fatty acids. However, in the case of polyamides reinforced with mineral fillers, such additives produce no marked improvement in the surface thereof.

We have now found, surprisingly, that polyamide molding compositions which contain, as well as from 10 to 70% by weight of a

mineral filler, from 0.1 to 2.0% by weight of a metal salt of a long-chain carboxylic acid (i.e. a carboxylic acid of 8 to 20 carbon atoms) and also from 0.5 to 4.0% by weight of a lactam, all these percentages being based on the total molding composition, may be worked to shaped articles having excellent surfaces.

Salts of calcium, strontium, barium, zinc and aluminum with carboxylic acids of from 8 to 20 carbon atoms, preferably stearic acid are examples of metal salts which may be used. Lactams of from 4 to 12 carbon atoms, preferably caprolactam, are examples of lactams which may be used.

Preferred polyamides are partially crystalline polymers which may be prepared by polycondensation or polyaddition from ω -amino-carboxylic acids or the corresponding lactams or from aliphatic and/or aromatic diamines with aliphatic and/or aromatic dicarboxylic acids. We particularly prefer polycaprolactams (nylon 6) having a relative viscosity of from 2 to 5.0 and polymers of hexamethylene diamine and adipic acid (nylon 6,6) having a relative viscosity of from 2.2 to 5.4, measured in both cases according to DIN 53,727 in 96% sulfuric acid (concentration 1.0 g/100 ml of solution at 25°C). When the polyamides are produced by polyaddition of caprolactam, the reaction generally proceeds to a conversion of only about 90%. Usually, the residual monomers are then removed by extraction. Thus commercial polycaprolactam is believed to contain less than 0.5% by weight of monomeric caprolactam.

Natural and synthetic fillers such as calcium carbonate, magnesium carbonate, kaolin, anhydrous aluminum silicates, aluminum oxides, talcum, silica flour and similar silicate-base compounds may be used as the mineral filler. They generally have average particle sizes of less than 100 μ and preferably of from 1 to 40 μ . The l/d ratio is generally below 10:1 and preferably below 4:1. The fillers may be treated with adhesion-promoting substances such as organosilanes and preferably aminopropyl triethoxysilane. The

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amount of filler in the molding compositions is preferably from 20 to 40%, by weight.

5 The molding compositions may additionally contain conventional additives such as stabilizers, pigments and flame-protectants (e.g. as proposed in German Published Application 1,808,130).

10 Incorporation of the surface-improvers proposed according to the invention may be carried out in conventional manner together with the fillers, e.g. by blending with the polyamides and melting in an extruder. Alternatively, and preferably in the case of polycaprolactam, monomer-free extracted polymer may be blended with non-extracted polymer (having a monomer content of from 9 to 10% by weight) in the desired proportions, the mixture then being processed with the other ingredients.

15 20 The following Example illustrates the invention.

EXAMPLE.

The premixed amounts of polyamide, filler and lubricant listed in the Table below are melted in a single-shaft extruder and homogenized. The polymer melt is extruded through a die and the extrudate is granulated and then injection molded to small test boxes. The Table lists the injection temperatures at which the surface of the finished article is satisfactory, i.e. glossy.

25 30 Tests *c*, *e*, *g* and *k* are within the scope of the invention, the remainder of the tests being comparative. At the processing temperatures given in tests *c*, *e*, *g* and *k* there is no degradation of the polymer, but in the comparative tests discoloration and marked appearance of fins are to be observed at said temperatures.

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TABLE

Test	Polymer	Filler	Additive	Temperature (°C) at or above which a good surface is obtained
a	nylon 6	30% of chalk	—	300
b	0.5% of Zn stearate	295
c	0.5% of Zn stearate and 2.0% of caprolactam	260
d	..	30% of chalk treated with calcium stearate	—	300
e	0.5% of Zn stearate and 2.0% of caprolactam	260
f	..	30% of calcined alumina	—	290
g	0.3% of calcium stearate and 2.5% of caprolactam	268
h	nylon 6,6	30% of silica flour treated with γ -amino-propylsilane as adhesion promoter	—	no good surface obtainable
i	0.5% of zinc stearate	310
k	0.5% of zinc stearate and 2.0% of caprolactam	280

Notes: All percentages given in the Table are percentages by weight based on the total molding composition. The chalk treated with calcium stearate used in Tests *d* and *e* contains 0.2% by weight of calcium stearate based on the chalk.

TEST
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WHAT WE CLAIM IS:—

1. A molding composition based on a polyamide and containing from 0.1 to 2.0% by weight of a metal salt of a carboxylic acid of 8 to 20 carbon atoms, from 0.5 to 4.0% by weight of a lactam, and from 10 to 70% by weight of a mineral filler, all these percentages being based on the total molding composition. 5 2.2 to 5.4, the relative viscosities being measured at 25°C on a 1.0g/100 ml solution in 96% sulfuric acid. 35

10 2. A molding composition as claimed in claim 1 wherein a salt of calcium, strontium, barium, zinc or aluminum with a carboxylic acid of 8 to 20 carbon atoms is used as metal salt. 40

15 3. A molding composition as claimed in claim 1 or 2 wherein a stearate is used as metal salt. 45

20 4. A molding composition as claimed in any of claims 1 to 3 wherein a lactam having from 4 to 12 carbon atoms is used. 50

25 5. A molding composition as claimed in claim 1 containing from 0.2 to 1.0% by weight of calcium stearate or zinc stearate as metal salt and from 1.5 to 2.5% by weight of caprolactam as lactam. 50

30 6. A molding composition as claimed in any of claims 1 to 5 wherein the polyamide is a polycaprolactam having a relative viscosity of from 2 to 5.0 or a polyhexamethylene-adipamide having a relative viscosity of from

7. A molding composition as claimed in any of claims 1 to 6 wherein calcium carbonate, magnesium carbonate, kaolin, anhydrous aluminum silicate, aluminum oxide, talcum or silica flour is used as mineral filler. 35

8. A molding composition as claimed in any of claims 1 to 7 containing 20 to 40% by weight of mineral filler based on the total molding composition. 40

9. A molding composition as claimed in any of claims 1 to 8 wherein the filler is treated with an organosilane as adhesion-promoting substance. 45

10. A molding composition substantially as hereinbefore described with reference to tests c, e, g and k of the foregoing Example. 50

11. Shaped articles manufactured from molding compositions as claimed in any of claims 1 to 10. 50

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